

U.S. Patent Appln. S.N. 10/069,145  
AMENDMENT

PATENT

REMARKS

This Amendment cancels claims 9 and 13, rewrites claims 8 and 12, adds new claim 17, and makes editorial changes to the specification. The tetraethoxysilane feature of claims 8 and 12 is taken from claim 9. New claim 17 is supported by page 15, lines 5-24. Claims 8, 10-12 and 15-17 are pending.

This Amendment overcomes the objection to the Amendment filed July 7, 2005. More particularly, claim 8 has been amended by deleting the phrase "up to 25 mol-%". Reconsideration and withdrawal of the new matter objection are earnestly requested.

This Amendment overcomes the 35 U.S.C. § 112, first paragraph, rejection of claims 8-13, 15 and 16. Independent claims 8 and 12 have been amended by replacing "tetraalkoxysilane" with --tetraethoxysilane--. The specification provides a written description of the presently-claimed composition and method. See, for example, page 6, lines 8-15 of the specification. Reconsideration and withdrawal of the 35 U.S.C. § 112, first paragraph, rejection of claims 8-13, 15 and 16 are earnestly requested.

This Amendment cancels claim 13. Reconsideration and withdrawal of the objection to claim 13 are earnestly requested.

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The 35 U.S.C. § 103(a) rejection of claims 8-11 over U.S. Patent No. 5,858,280 to Zhang et al. in view of U.S. Patent No. 5,804,318 to Pinchuk et al. is respectfully traversed. The claimed invention is a biodegradable silica xerogel composition which contains heparin or a related biologically active acidic polysaccharide. The silica xerogel is derived from tetraethoxysilane, with part of the tetraethoxysilane being replaced by an alkylsubstituted alkoxy silane.

The Patent Office concedes that Zhang et al. fails to disclose heparin or a related biologically active acidic polysaccharide in combination with a silica gel (Official Action, page 8, lines 8-9). Yet, the Patent Office claims that Zhang et al.'s disclosure of methyl-modified silica gel doped with optically functional substances discloses modified silica gels containing a biologically active agent. See page 5, lines 3-6 and 9-13 of the Official Action.

Nowhere does Zhang et al. define "optically functional substances". The two references cited by Zhang et al. report the embedding of rhodamine 6G in a silica matrix<sup>1</sup> and the introduction

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<sup>1</sup>Avnir et al., "The Nature of the Silica Cage as Reflected by Spectral Changes and Enhanced Photostability of Trapped Rhodamine 6G," 88 J. Phys. Chem. 5956 (1984) (copy attached).

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of an organic dye molecule, 1,4-dihydroxyanthraquinone, into an amorphous silica followed by photochemical hole burning.<sup>2</sup> Neither reference discloses or suggests the incorporation of a biologically active agent, much less heparin or a related biologically active acidic polysaccharide, in a silica gel.

There is simply no motivation or suggestion in Zhang et al. to incorporate heparin (or its related biologically active acidic polysaccharide) into Zhang et al.'s transparent methyl-modified silica gel. The Examiner is respectfully requested to either (1) withdraw her assertion that Zhang et al.'s incorporation of optically functional molecules discloses or suggests the inclusion of a biologically active agent into a silica gel in the next Patent Office communication, (2) identify by column and line number, where such disclosure may be found in Zhang et al., (3) provide other evidence that one of ordinary skill in the art would understand the doping of a silica xerogel with optically functional molecules discloses the inclusion of a biologically active agent, or (4) if the assertion is based on facts within the personal knowledge of the Examiner, she is requested to supply an affidavit describing such personal knowledge pursuant to 37 C.F.R. § 1.104(d)(2).

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<sup>2</sup>Tani et al., "Photochemical Hole-Burning Study of 1,4-dihydroxyanthraquinone Doped in Amorphous Silica Prepared by Alcoloholate Method," 58 J. Appl. Phys 3559 (1985) (copy attached).

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The deficiencies of Zhang et al. are not remedied by the additional disclosure of Pinchuk et al., which also fails to disclose or suggest that heparin or a related biologically active acidic polysaccharide can be incorporated into sol-gel derived xerogel derived from tetraethoxysilane which has been co-hydrolyzed with an alkylsubstituted alkoxy silane, or that heparin may be controllably released from the xerogel. Instead, Pinchuk et al. discloses a surface coating comprising a non-silica hydrogel containing pendant primary and tertiary amine groups (Col. 3, lines 26-29).

Pinchuk et al. is cited to show an epoxy-functionalized, silane primed catheter dipped into a hydrogel solution containing 2% heparin. However, the silane coupling agent is used only for silylation of the surface of the material to be coated. The coating itself is not made of sol-gel derived silica xerogel derived from tetraalkoxysilane.

Pinchuk et al. expressly teaches the anticoagulant agent is bound to quaternary ammonium cations present in its hydrophilic polymer matrix (non-silica) hydrogel. See Col. 3, lines 31-33, Col. 5, lines 13-15 and Fig. 4. There is no teaching or suggestion that heparin may be controllably released from a sol-gel derived silica xerogel derived from tetraethoxysilane. Accordingly, there

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is no motivation or suggestion to combine the references as proposed by the Patent Office.

The results of dissolution experiments on the claimed silica xerogel suggest heparin is released by silica matrix erosion and diffusion (Specification, page 13, lines 6-16). Dissolution of heparin by diffusion suggests that the claimed silica xerogel contains the biologically active agent by physical occlusion rather than by chemical bonding. In contrast, Pinchuck et al. chemically bonds heparin to the quaternary ammonium groups on the surface of its coated substrate (Col. 5, lines 12-18).

One of ordinary skill in the art, seeking a biodegradable silica xerogel composition which is capable of controlled release of heparin, would not be led to the claimed composition by Zhang et al. and Pinchuk et al. Reconsideration and withdrawal of the obviousness rejection of claims 8-11 over Zhang et al. in view of Pinchuk et al. are earnestly requested.

The 35 U.S.C. § 103(a) rejection of claims 8-11 over Kuncova et al., 60 Collect.Czech.Chem.Commun. 1573 (1995) in view of Pinchuk et al. is respectfully traversed. A feature of the claimed biodegradable composition is the partial replacement of tetraethoxysilane with an alkylsubstituted alkoxy silane. A second feature is the presence of heparin or a related biologically active

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acidic polysaccharide. The inventors have discovered a biodegradable composition comprising a silica xerogel which is capable of controlled release heparin or a related biologically active acidic polysaccharide.

The combination of Kuncova et al. and Pinchuk et al. fails to raise a *prima facie* case of obviousness against the claimed composition. Kuncova et al. is directed to the immobilization of lipase into an organic-inorganic matrix, and thus fails to disclose or suggest a biodegradable composition for controlled release of heparin or a related biologically active acidic polysaccharide from a carrier. Moreover, Kuncova et al. fails to disclose the partial replacement of tetraethoxysilane with an alkylsubstituted alkoxy silane.

The deficiencies of Kuncova et al. are not remedied by the additional disclosure of Pinchuk et al., which merely discloses a non-silica hydrogel bound to a surface to be coated by a silane coupling agent, and the chemical bonding of heparin to the quaternary ammonium groups on the surface of Pinchuk et al.'s substrate. One of ordinary skill in the art would not be led to the prepare a silica xerogel in which heparin (or a related biologically active acidic polysaccharide) is physically embedded and which can be controllably released from the silica matrix.

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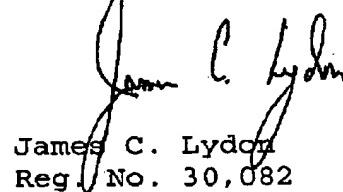
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Reconsideration and withdrawal of the obviousness rejection of claims 8-11 over Kuncova et al. in view of Pinchuk et al. is respectfully requested.

It is believed this application is in condition for allowance. Reconsideration and withdrawal of all rejections of claims 8-11, and issuance of a Notice of Allowance directed to claims 8, 10-12 and 15-17, are earnestly requested. The Examiner is urged to telephone the undersigned should she believe any further action is required for allowance.

It is not believed any fee is required for entry and consideration of this Amendment. Nevertheless, the Commissioner is authorized to charge our Deposit Account No. 50-1258 in the amount of any such required fee.

Respectfully submitted,



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Enclosures:

- Avnir et al., 88 J. Phys. Chem. 5956 (1984)  
Tani et al., 58 J. Appl. Phys. 3559 (1985)

# Photochemical hole-burning study of 1,4-dihydroxyanthraquinone doped in amorphous silica prepared by alcoholate method

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(Received 30 March 1985; accepted for publication 25 July 1985)

Preparation of amorphous silica doped with organic dye molecules, 1,4-dihydroxy-anthraquinone, and the observation of the amorphous structure of this system by photochemical hole burning using the dye molecules as a spectral probe are reported. The various kinds of organic molecule-doped inorganic glassy materials are obtained with the alcoholate method. The appearance of the photochemical hole in this system shows the molecular dispersion of the dye molecules in the matrix without cracking or decomposition. The burning yield,  $1.2 \times 10^{-4}$ , is the same as that observed in organic glasses. The intrinsic linewidth,  $0.9 \text{ cm}^{-1}$  at zero burning time limit, the burning-time dependence and the annealing effects on the hole profile were observed and compared with those in the alcoholic organic glass. It is suggested that the nearest-neighbor structures around quinizarin molecules consist of some hydroxyl groups. The matrix cages seem to be fairly tight and rigid in comparison with those of the alcoholic glass. The possibility that the quinizarin molecule or molecules are embedded within the pore of amorphous  $\text{SiO}_2$  with some amount of solvent molecules, mainly ethanol or water, seems to be excluded. The annealing effects of the burned hole indicate that there exist two kinds of mechanisms which dominate the temperature dependence of the linewidth in the present system. One is already dominant below about 27 K which gives rise to the reversible behavior in the linewidth with temperature, and the other becomes effective above 27 K and is irreversible with temperature cycling. Some discussions are given on the origin of these relaxation mechanisms in this system which are inherent in the structure of amorphous materials.

## I. INTRODUCTION

Among the techniques used to prepare oxide glasses the alcoholate method,<sup>1,2</sup> a kind of sol-gel method, has the following advantage over conventional techniques; that is, it gives glasses at fairly low temperatures (1200 °C at most). This enables us to chemically prepare glasses of new composition which could not be obtained with ordinary high-temperature melt quenching.

From the point of view of material science, structural disorder and its effects on the electronic structures have been an important problem in amorphous solids. Ever since the anomalous contribution to the specific heat of silica glass was reported below 1 K,<sup>3</sup> extensive experimental efforts have been devoted to understand the dynamical aspects of disordered solids. Although the observed phenomena seem to be consistent with the theoretical model<sup>4,5</sup> based on the existence of two-level systems (TLS's), the microscopic nature of TLS's is still not understood.

In our attempt to gain further insight into the structures and dynamical properties of amorphous solids at low temperatures, we tried to introduce photosensitive "organic dye molecules" into the "inorganic silica glass matrix" and to probe the glass structures by photochemical hole-burning spectroscopy. Although silica glass is a typical amorphous oxide, the doping of thermally dissociative components in it has never been realized due to its high melting temperature.

Adopting the method stated above, however, we successfully obtained the organic molecule-doped inorganic glassy materials as a molecular dispersion, which is stable at ambient. The burned hole profile in the system described below is demonstrated in Fig. 1, which shows a sharp zero-phonon hole at the same wavelength of the laser light and a broad side hole at the longer wavelengths. The appearance of a persistent hole is the most convincing evidence of the molecular dispersion in the solid. Some information on the structure of the matrix cage can also be obtained from the profiles of hole spectra.

Photochemical hole burning (PHB) is a kind of photo-bleaching technique which utilizes a site selective photo-induced reaction to form a persistent hole in the inhomogeneously broadened absorption band by laser light irradiation.<sup>6-9</sup> It is a high-resolution molecular spectroscopy which enables one to observe the homogeneous line profile of site-selected molecules. It has attracted wide attention since the possible application was proposed for a frequency selective optical data storage system with more than  $10^3$  times higher than the upper limit of the storage density of the present optical disk system.<sup>10,11</sup> Our new material, the photoreactive molecule or molecular aggregates doped in the glassy silica matrix, is a good candidate as a storage material due to the rigidity and stability of the matrix in comparison with organic matrices.

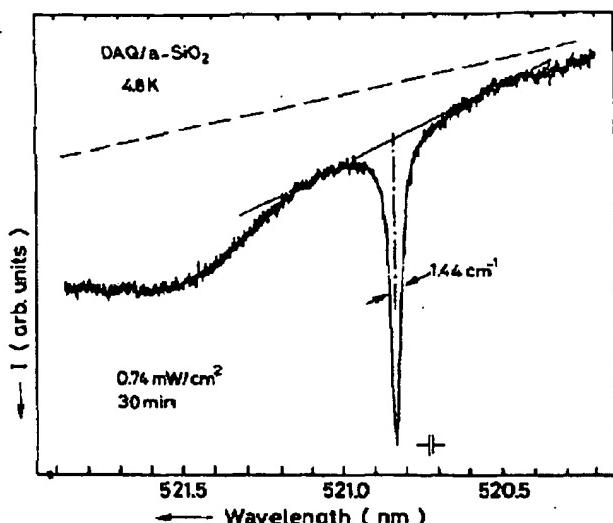


FIG. 1. Photochemical hole spectrum burned at 4.8 K. Sample is 1,4-dihydroxyanthraquinone doped in the amorphous silica. Laser light (520.83 nm) of 0.74 mW/cm<sup>2</sup> was irradiated into the 0-0 excitation band for 30 min. Broken line indicates the position of absorption spectrum before burning. Resolution of the measurement (0.08 Å) is indicated in the figure.

In the following, after the preparation of the amorphous silica doped with organic dye molecules is described, we present the results on the PHB observation at liquid-helium temperatures together with the absorption and fluorescence spectra measured at room temperature. Qualitative discussions are given on these observations.

## II. EXPERIMENTS

### A. Sample preparation

We used 1,4-dihydroxy-9,10-anthraquinone (DAQ, Quinizarin) as the photoreactive molecules and tetraethoxysilane, Si(O<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, as the starting material for silica gel glass formation. Quinizarin was purified by the recrystallization from an ethanol/benzene mixed solvent (1:2 in volume) at 70 °C. The residual solvents were removed by drying at 60 °C for 1 h under evacuation ( $10^{-2}$  Torr). Quinizarin was dissolved into the spectroscopic grade ethanol to the concentration of  $10^{-6}$  mol/mol. The organic molecules are dissolved at first in the solvent then the tetraethoxysilane. A quinizarin/ethanol solution of 11.4 cm<sup>3</sup> in volume, Si(O<sub>2</sub>H<sub>5</sub>)<sub>4</sub> of 10.0 cm<sup>3</sup> and distilled water of 3.7 cm<sup>3</sup> were measured into the 100-cm<sup>3</sup> beaker and mixed together to a homogeneous solution. The hydrolysis for gelling was carried out at 60 °C with 0.1-cm<sup>3</sup> HCl (pH = 5) as the catalyst. The gel so obtained was then kept at 40 °C with 30% relative humidity for three days. The resultant solid is stiff, transparent, and yellow-colored noncrystalline material with smooth surfaces. Quinizarin seems to be dissolved in the solid homogeneously without macroscopic segregation. The dimension of the disk is 28 mm in diameter and 3 mm in thickness. The acidic, or at least neutral, hydrolysis of Si(O<sub>2</sub>H<sub>5</sub>)<sub>4</sub> is a necessary condition for the formation of monolithic silica gel, which is different from the results of Avnir *et al.*<sup>12</sup> Under the basic con-

dition the syneresis occurs quite often and the gel takes micrograin structure. The organic molecules are likely to be expelled with solvents from the grains during condensation. The detailed explanation on the preparation of the organic molecule-doped inorganic amorphous silica and its relatives are discussed elsewhere.<sup>13</sup>

The quinizarin/amorphous SiO<sub>2</sub> system (DAQ/a-SiO<sub>2</sub>) formed above was separated to several pieces with diamond cutter and used for measurement without further sample treatment such as polishing.

### B. Instruments

The newly developed DAQ/a-SiO<sub>2</sub> material was evaluated by two optical methods. One is the absorption and fluorescence spectra observed at room temperature in the visible wavelength region and the other is the PHB spectroscopy at liquid-helium temperatures. In particular, the latter is useful to get the microscopic information on the structure and interaction between the photoreactive molecules and their surroundings.

The absorption spectra were measured with conventional spectrophotometer (model 323, Hitachi) and the fluorescence spectra were obtained with a fluorescence spectrophotometer (MPF-4, Hitachi). The PHB experiments were performed with a cw krypton ion laser (CR-3000K, Coherent) operated at 520.83 nm for burning holes at low temperatures. The samples were cooled down to liquid-helium temperature region with the continuous flow temperature-variable cryostat (CF-204, Oxford). The burned holes were detected at various temperatures by measuring the transmission spectra with 1-m monochromator (1704, Spex). A grating with a dispersion of 8 Å/mm and slit width of 10 μm give the resolution of about 0.08 Å. The monochromatic light from 150-W tungsten/halogen lamp was focused through the sample onto the photomultiplier (R376, Hamamatsu). Signals were detected phase sensitively and recorded on the strip-chart recorder.

## III. RESULTS AND DISCUSSIONS

The absorption spectrum of DAQ/a-SiO<sub>2</sub> system in the visible region measured at room temperature is shown in Fig. 2(a), curve A. The spectrum of quinizarin in the solution of Si(O<sub>2</sub>H<sub>5</sub>)<sub>4</sub>/ethanol/water with HCl as a catalyst just after mixing (curve B) and that in 3:1 mixed solvent of ethanol and methanol (curve C) are also shown for comparison. The comparatively large background of curve A and its increase at shorter wavelength region is mainly due to the surface scattering of the sample. The fluorescence spectrum of DAQ/a-SiO<sub>2</sub> system and those of quinizarin in the other two solutions are shown in Fig. 2(b). As can be seen in the figure, the profiles of absorption spectra in DAQ/a-SiO<sub>2</sub> system resemble generally well those of quinizarin in the liquid solutions. Spectral profiles of fluorescence of quinizarin in the three media are almost equal to each other and show no dependence on the excitation wavelength ( $\lambda_{ex} = 280, 330$ , and 400 nm). These indicate that the quinizarin molecules are incorporated within the bulk of amorphous silica with-

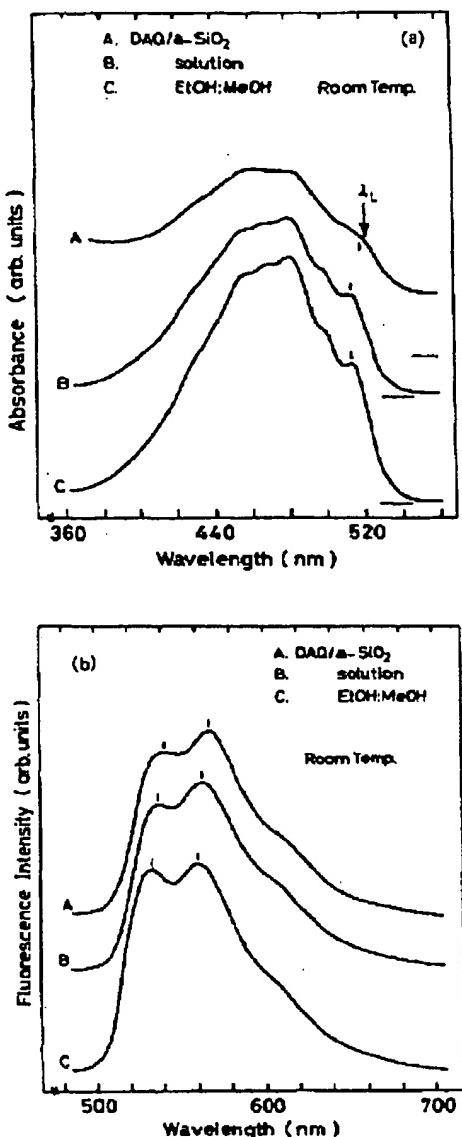


FIG. 2. Absorption (a) and fluorescence (b) spectra of quinizarin in amorphous silica measured at room temperature are shown in comparison with those in two solutions. In the figures, curve A corresponds to the spectrum in the amorphous silica, curve B in  $\text{Si}(\text{OC}_2\text{H}_5)_4$ /ethanol/water solution, curve C in ethanol/methanol 3:1 mixed solvent, respectively. In the absorption spectrum of DAQ/a-SiO<sub>2</sub>, wavelength of the laser light is indicated by  $\lambda_L$ .

out changing chemically. Moreover, assuming that the oscillator strength of the molecules is the same in the solutions and in the rigid matrix, the density of quinizarin molecules in the amorphous silica estimated from the curve A in Fig. 2(a) is almost equal to that calculated from the starting density simply by taking the volume contraction into account. This confirms further that the doped quinizarin molecules are

dispersed in the amorphous silica without cracking or decomposition.

There exist, of course, several differences among the spectra if examined more closely and some of them are noted below. In the absorption spectra, five vibrational structures are observed. Their positions are almost same in the alcoholic solvent and in the  $\text{Si}(\text{OC}_2\text{H}_5)_4$  solution. The solvation effect on quinizarin molecules seems to be effectively equal in both liquids. However, the spectrum of DAQ/a-SiO<sub>2</sub> system is different from these two. The vibrational structures are broadened and the 0-0 transition observed at 514 nm in the solutions is shifted to longer wavelength ( $\Delta\lambda \approx 7$  nm). The vibrational components in the fluorescence spectra are broader than those in the absorption spectra and only two peaks and one shoulder are distinguished. In this case, however, the change in the broadening from the liquids to the amorphous SiO<sub>2</sub> is not detectable. Another notable point in the fluorescence spectra is that the shift of the peaks towards longer wavelength occurs sequentially from alcoholic solvent through  $\text{Si}(\text{OC}_2\text{H}_5)_4$  solution to amorphous SiO<sub>2</sub> which is different from those in absorption spectra stated above. The total amount of the red shift from alcoholic solvent to amorphous SiO<sub>2</sub> is about 7 nm which is almost equal to that observed in the absorption spectra. But the shift from alcoholic solvent to  $\text{Si}(\text{OC}_2\text{H}_5)_4$  solution is about 4 nm, while the corresponding shift is almost zero in the absorption. Among these, the broadening of the vibrational structures observed in the absorption indicates that the nearest-neighbor structures around quinizarin molecules or the wall structure of the matrix cage is not so simple as the cluster structure of solvation in the solutions if we could compare with solvents. As for the shift of the spectrum observed, the polarity and conformational structure around quinizarin may be seriously affected. The formation of the cage during condensation and the rigidity should be examined carefully. We observed blue shifts of absorption and/or fluorescence spectra as well as red shifts in some other cases of organic functional molecules. The optical observations on the various kinds of organic molecule-doped amorphous SiO<sub>2</sub> systems will be reported elsewhere.<sup>14</sup>

The behavior of photochemical hole generation is discussed in the following. The hole is burned by the laser light irradiation with the intensity of  $0.74 \text{ mW/cm}^2$  at  $520.83 \text{ nm}$  in wavelength. Typical profiles of the hole growth at 4.8 K under successive burning times are shown in Fig. 3. An observable hole appears with a few seconds exposure at most and the wavelength is coincident with the laser light within the experimental accuracy. After two minutes of irradiation, a broad sidehole also appears at lower energy side of the sharp zero-phonon hole. The appearance of the phonon sideband means that an interaction is strong to some extent<sup>15</sup> between the electrons in the quinizarin and phonons in the surrounding matrix.

The mechanism of hole burning in DAQ/a-SiO<sub>2</sub> system seems to be photochemical in nature and not photophysical, judging from its burning yield (Table I). It is  $1.2 \times 10^{-4}$  and is equal to the one observed in the alcoholic glass, where the photochemical hole burning is considered to occur. Photophysical mechanism usually gives the yield of  $10^{-6}$  or less.<sup>16</sup>

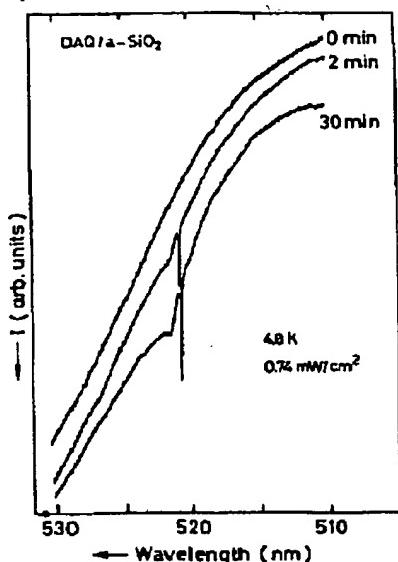


FIG. 3. Hole growth profile with increasing the burning time at 4.8 K. Burning conditions are the same as in Fig. 1.

Burning-time dependences of the zero-phonon linewidth are plotted in Fig. 4. The observed linewidth increases almost linearly with burning time and saturation broadening does not appear within the present experimental conditions. For short burning time  $t$ , the width of the hole  $\Gamma_h$  increases as<sup>17,18</sup>

$$\Gamma_h(t) = \Gamma_0 [1 + \sigma(I/\hbar\omega_L)\phi t]^{1/2}, \quad (1)$$

where  $\sigma$  is the absorption cross section,  $I$  and  $\omega_L$  the laser light intensity and frequency,  $\phi$  the photochemical yield,  $\alpha$  the Debye-Waller factor, and  $\hbar$  the Planck's constant. This model assumes phenomenologically a Lorentzian line shape of molecular absorption irrespective of its line broadening mechanism. The observed line shape of zero-phonon hole is almost Lorentzian as can be seen from Fig. 1. Adopting the model expressed in Eq. (1), the intrinsic linewidth  $\Gamma_0$  extrapolated to  $t = 0$  in this system is  $0.9 \text{ cm}^{-1}$  at 4.8 K.

The important properties of hole profiles appear in the behavior of linewidth with temperature change. We adopted here two kinds of thermal annealing procedures which affect the set of molecules site selected by the hole burning.<sup>18</sup> The hole was burnt at the base temperature (4.7–4.8 K). (1) The first procedure is a stepwise annealing where the temperature of the sample was raised in successive steps. The

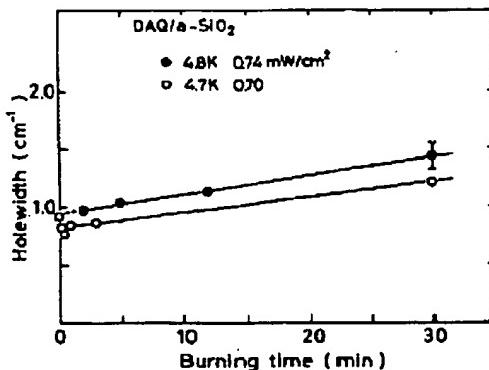


FIG. 4. Holewidth as a function of the successive burning time. Two sets of data were obtained at different runs on the same sample.

hole profiles were observed at the base temperature at first and then at every elevated temperature. (2) The second one is a cycle annealing where the temperature of the sample was raised to a prescribed temperature and, after being kept for more than five minutes, cooled again rapidly to the base temperature at each cycle. In the cyclic annealing, therefore, the hole profiles were all measured at the base temperature. The second procedure reveals the irreversible process, which may occur during the temperature cyclings and contribute to the hole profile, while the first one reveals both the reversible and irreversible process with increasing temperature.

The temperature change of the hole spectra obtained by stepwise annealing is shown in Fig. 5. The depth of zero-phonon hole decreases steeply with increasing temperature and almost disappears at 34.1 K. The data points in Fig. 6 (curve A) show the temperature change of the full width at half depth of hole spectra shown in Fig. 5. The solid line in Fig. 6 (curve A) is the fitted curve to the data points and is expressed as

$$\Gamma_h(t) = 1.2 + 1.22 \times 10^{-2} T^{1.7} [\text{cm}^{-1}], \quad (2)$$

which is almost proportional to the square of the temperature.

The most noticeable property observed in DAQ/a-SiO<sub>2</sub> system appears in the temperature change obtained by the cycle annealing. The observation of hole spectra at base temperature was possible even after the cycle annealing as high as 67 K. The linewidth of the hole almost perfectly recovers under the temperature cycling up to 27 K as is seen in Fig. 6 (curve B). However, the linewidth begins to grow at temperatures higher than 30 K and the irreversible component increases rather slowly with raising the cycle temperatures. These behaviors are quite different from those observed in the organic systems like ethanol/methanol glass, where the irreversible change obtained by the cycle annealing is large and increases steeply with cycle temperatures and the hole cannot be observed after the annealing above 30 K.<sup>19</sup>

It should be noted here that the appearance of the flat portion in Fig. 6 (curve B) below 27 K is not due to any experimental artifact such as the laser spectral linewidth or the spectral resolution of the monochromator. The latter is about 0.08 Å (0.3 cm<sup>-1</sup>) as is described in the experimental

TABLE I. Quantum yields of PHB ( $\phi$ ), Debye-Waller factors ( $\alpha$ ), and absorption cross sections ( $\sigma$ ) of quinizarin in the matrices.

matrix	$\phi$ (4.8 K)	$\alpha$ (4.8 K)	$\sigma^*$ (cm <sup>2</sup> )
a-SiO <sub>2</sub>	$1.2 \times 10^{-4}$	0.20	$6.4 \times 10^{-15}$
EtOH/MeOH	$1.2 \times 10^{-4}$	0.13	$6.4 \times 10^{-15}$

\*Both  $\sigma$ 's are the values in the solutions at room temperature.

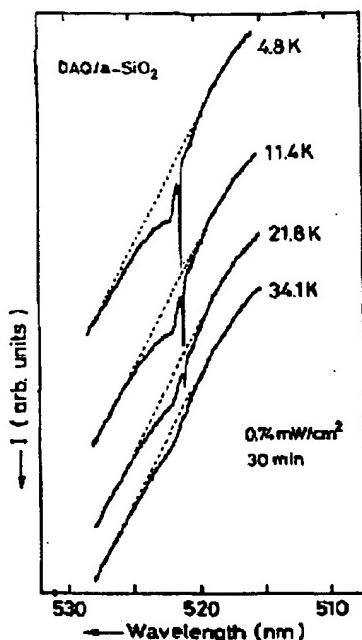


FIG. 5. Temperature change of the hole spectra under the *stepwise* annealing (see text). Hole was burnt at 4.8 K at first and the spectra was measured at each elevated temperature successively.

section and the former is several times narrower. Actually, the direct observation of the spectrum of the laser light used for the burning satisfied these properties sufficiently.

As is mentioned earlier, the frequency-selective photochemistry of PHB involves only a specific subset of photo-reactive molecules without affecting the other subsets in the matrix. Therefore, the appearance of holes indicates that quinizarin molecules are dispersed and sufficiently isolated each other in the amorphous SiO<sub>2</sub> matrix.

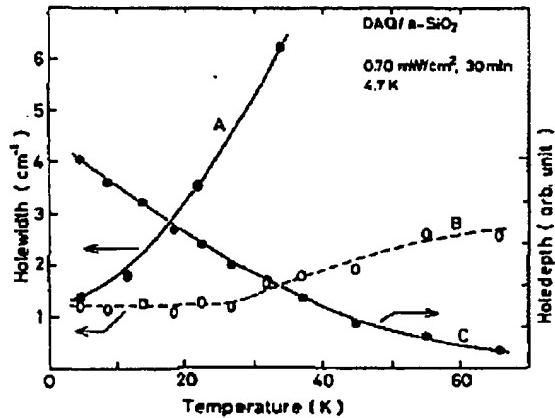


FIG. 6. Data points in curve A show the temperature dependence of the holewidth under the *stepwise* annealing shown in Fig. 5, while solid line in curve A is the fitted curve expressed in Eq. (2). Data points in curve B show the annealing temperature dependence of the holewidth under the *cycle* annealing. In curves B and C, the data points are plotted as a function of cycle annealing temperatures and hole spectra were all measured at the base temperature (see text).

The burning-time dependence of the zero-phonon holewidth shown in Fig. 4 can be understood by the simple model expressed in Eq. (1). The parameters which are used in the present analysis are listed in Table I. The corresponding values in case of ethanol/methanol are also shown in the table for comparison. The hole-burning yield  $\phi$  is estimated from the intensity of zero-phonon hole spectrum under conditions where the phonon sidehole is not yet observable. The value  $\phi$  in amorphous SiO<sub>2</sub> is same as in the alcoholic glass. The Debye-Waller factor  $\alpha$  is roughly estimated from the spectra shown in Fig. 4. The absorption cross section  $\sigma$  is deduced from the absorption spectra in the Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> solution at room temperature just after mixing. This value is same as in the alcoholic solvent at room temperature and we assume that it also does not change in the rigid a-SiO<sub>2</sub> matrix at low temperatures. From the laser intensity  $I$ , its frequency  $\omega_L$ , and the value listed in Table I, the slope of the time dependence in Eq. (1) is estimated as  $2.3 \times 10^{-2} \text{ min}^{-1}$ , which agrees well to the observed value of  $1.7 \times 10^{-2} \text{ min}^{-1}$  within our experimental accuracy.

Interestingly, though the slope at short burning time region observed in the ethanol/methanol matrix is more than one order of magnitude larger<sup>19</sup> than in the amorphous SiO<sub>2</sub>, the extrapolated holewidth  $\Gamma_0$  is roughly the same in both matrices ( $1.1 \text{ cm}^{-1}$  in the former and  $0.9 \text{ cm}^{-1}$  in the latter).  $\Gamma_0$  reflects the optical dephasing and/or relaxation processes which take place during the excitation. In other words,  $\Gamma_0$  should depend upon the environments of the molecules. Therefore, the fact that  $\Gamma_0$ 's in the amorphous SiO<sub>2</sub> and ethanol/methanol matrix are almost equal to each other suggests that at least the nearest-neighbor structure of the quinizarin in the amorphous SiO<sub>2</sub> is effectively the same as in the alcoholic matrix. We have assumed in this context that the photochemical reaction for hole formation is common in both cases.

In relation to the structure of the nearest neighbors, the existence of micropores in the gel glasses prepared with HCl as catalyst,<sup>20</sup> seems noteworthy. The size distribution has two peaks around 20 and 70 Å in case that the heat treatment temperatures are lower than 400 °C. As our system is not heat treated higher than 60 °C, it must also contain a lot of pores. Even the smaller size of pore seems to be sufficient to accommodate the dye molecule. If the surface of the pores consists of the hydrogen-bonded silanol groups,<sup>20</sup> the nearest-neighbor surroundings of quinizarin in the amorphous SiO<sub>2</sub> seems to resemble the one in the alcoholic matrix: that is, hydroxyl nature of the surroundings. However, the different behaviors in the burning time dependence and the annealing effects on the hole profiles from those observed in the alcoholic glass suggest that the quinizarin molecules are not enclosed within bulk layer of ethanol and water molecules, the assemblies of which being embedded in the amorphous SiO<sub>2</sub>, but are almost directly embedded in the inorganic matrix. Of course, we cannot exclude the possibility that one or a few molecules of ethanol or water may be joined with a quinizarin molecule in a cage of the amorphous SiO<sub>2</sub> matrix.<sup>24</sup>

As for the optical properties in the disordered solids, some theoretical models were proposed recently to explain

the temperature dependences of optical linewidth, which take into account the interaction between the dye molecules (or impurity centers) and phenomenological TLS's which are inherent to the amorphous state. Among these, only Lyo and Orbach's model<sup>21</sup> predicts a homogeneous linewidth proportional to the square of the temperature at low temperatures. The experimental result shown in Fig. 6 (curve A), expressed as in Eq. (2), seems to be interpreted by the prediction of the Lyo and Orbach's model. Phonon-induced fluctuations of the TLS in thermal equilibrium give rise to an interruption of the phase of the quinizarin via the electrostatic interaction. Here we have to take into account the behavior of holewidth under the cycle annealing. As is shown in Fig. 6 (curve B), the irreversible changes in the holewidth were scarcely observed in the temperature cyclings up to about 27 K. These observations may indicate that there exist certain TLS's in amorphous SiO<sub>2</sub> matrix working for the reversible line broadening process in the observed temperature region (5–27 K) but they do not contribute to the hysteresis.

The appearance of irreversible annealing effect above 27 K is the most notable feature in the DAQ/ $\alpha$ -SiO<sub>2</sub> system. This anomaly reveals itself in the temperature change of the holewidth only and not of the hole depth, as can be seen from Fig. 6 (curves B and C). This suggests that the hole filling backward reaction of photoproducts is thermally induced monotonically and that the anomaly should be related to the relaxation processes which give rise to further broadening of the hole in addition to the reversible one due to the change in the ground-state distribution of the sites. The microscopic origin of these processes cannot be identified at present. So far, we simply propose two possible mechanisms by intensive review of the literature, which should be verified through further experimental investigations.

In the ultrasonic attenuation,<sup>22–24</sup> the relaxation process, which begins to increase its contribution at about 30 K and seems to be most effective at around 60 K, is also observed in the silica glass. Anderson and Bömmel assumed that in vitreous silica oxygen atoms can move perpendicularly to their bond direction at around 60 K.<sup>22</sup> This relaxation process can be one possible origin of the anomaly in the holewidth above 27 K.

In the amorphous SiO<sub>2</sub> matrix, on the other hand, there remains considerable amount of water and organic groups (—OC<sub>2</sub>H<sub>5</sub>, —OH, etc.) due to insufficient polymerization. Residual water is confirmed by the infrared absorption measurement,<sup>20</sup> for instance. These residual groups may be stable in the local minima of their potential surfaces at low enough temperatures, but will begin to rotate or move over the barriers to be distributed to other extrema at elevated temperatures. This reorientation of residual organic groups in the matrix may cause the irreversible change of the local fields at the dye molecules when the system is quenched to the base temperature after cycle annealing and results in the hysteresis as observed in the experiments. For example, the reorientation of ester ethyl groups in polyethyl methacrylate occurs in the temperature region from 30 to 60 K, which is confirmed by the internal friction,<sup>25</sup> nuclear magnetic resonances,<sup>26</sup> dielectric and ultrasonic observations,<sup>27</sup> if the com-

parison with the polymers is desired. Further experiments on the amorphous SiO<sub>2</sub> matrix in which the amount of the residual groups and/or water are controlled are of utmost importance.

These two mechanisms which are both dominant above 27 K, are considered to be induced by thermally activated hopping process rather than phonon-assisted tunnelling. Below 27 K, there seems to exist a reversible hole broadening mechanism. From the burning-time behavior at 4.8 K and the cycle annealing properties of the holewidth, the nature is considered not like the TLS's proposed in the alcoholic glass<sup>18</sup> but like those characteristic in the silica glass. In the silica glass prepared by the conventional technique the anomaly in the specific heat observed in very low temperatures seems to disappear above 1 K.<sup>3</sup> This anomaly is accepted as a typical evidence of the existence of TLS in the glass. Though the impurities or some detailed structures being different in the two systems, it seems natural to consider the TLS's in the silica glass mentioned above also exist in the present amorphous SiO<sub>2</sub> system.

As related systems to the DAQ/ $\alpha$ -SiO<sub>2</sub>, the DAQ/boric acid glass<sup>18</sup> and free-base porphin/boric acid glass<sup>28</sup> seem to be interesting. Though the detailed temperature dependence is not clear in the former, the linewidth of the hole seems almost equal to that of the DAQ/ $\alpha$ -SiO<sub>2</sub> system. The boric acid glass usually contains lots of the hydroxyl groups and is called a hydrogen-bonded glass. Therefore, it is possible that the nearest neighbor structures around quinizarin are effectively equal in both cases by the same reason discussed before.

We add briefly the comment on the sidehole.<sup>15</sup> The appearance of the sidehole indicates that the coupling between the molecules and the low-energy excitations, mainly phonons, in the matrix is not negligible. Assuming single phonon mode is dominant, Huang-Rhys factor (*S*) deduced from Debye-Waller factor by the relation  $\alpha = \exp(-S)$  and the dominant phonon energy are roughly estimated as 1.6 and 13 cm<sup>-1</sup>, respectively, from the spectra shown in Figs. 1, 3, and 5. The *S* value of 1.6 larger than 1.0 indicates that the coupling is intermediate in strength but weaker than in ethanol/methanol glass in our data (*S* = 2.0).<sup>19</sup>

Yet another comment is on the DAQ/ $\alpha$ -SiO<sub>2</sub> system as an aspect of new hybrid organic-inorganic materials both from fundamental and practical points of view. Adopting the alcoholate method, we can introduce various organic molecules<sup>13</sup> into the inorganic oxide glasses with variety of compositions such as SiO<sub>2</sub>, GeO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, and their mixtures. These organic molecule-doped inorganic glassy materials in the molecular dispersion may provide a new field in the material science. A part of its possibility has been shown in our present experiment. The materials will be promising also for various kinds of optical and optoelectronic applications including the PHB memory due to the advantage of the rigidity and stability of the inorganic glassy matrices which keep alive the function of organic molecule and molecule itself. It can also be a milestone for the future molecular electronic materials. The materials including the one described in this paper as well as the applications are Japanese patent (September 19, 1984) pending.

## ACKNOWLEDGMENTS

The authors express their thanks to Dr. U. Itoh and Dr. Y. Tanabe for informative discussions. They also are grateful to Dr. H. Anzai for his kind introduction to the purification of quinizarin.

- <sup>1</sup>H. Dislich, Angew. Chem. Int. Ed. 10, 363 (1971).
- <sup>2</sup>S. Sakka and K. Kamiya, J. Non-Cryst. Solids 42, 403 (1980).
- <sup>3</sup>R. C. Zeller and R. O. Pohl, Phys. Rev. B 4, 2029 (1971).
- <sup>4</sup>P. W. Anderson, B. J. Halperin, and C. M. Varma, Philos. Mag. 25, 1 (1972).
- <sup>5</sup>W. A. Phillips, J. Low Temp. Phys. 7, 351 (1972).
- <sup>6</sup>A. A. Gorokhovskii, R. K. Kaali, and L. A. Rebane, JETP Lett. 20, 216 (1974).
- <sup>7</sup>B. M. Kharlamov, R. I. Personov, and L. A. Bykovskaya, Opt. Commun. 12, 191 (1974).
- <sup>8</sup>L. A. Rebane, A. A. Gorokhovskii, and J. V. Kikas, Appl. Phys. B 29, 235 (1984).
- <sup>9</sup>J. Friedrich and D. Haarer, Angew. Chem. Int. Ed. Engl. 23, 113 (1984).
- <sup>10</sup>G. Castro, D. Haarer, R. M. MacFarlane, and H. P. Trommsdorff, U. S. Patent 4, 101, 976 (1978).
- <sup>11</sup>A. R. Gutierrez, J. Friedrich, D. Haarer, and H. Wolfrum, IBM J. Res. Dev. 26, 198 (1982).
- <sup>12</sup>D. Avnir, D. Levy, and R. Reisfeld, J. Phys. Chem. 88, 5956 (1984).
- <sup>13</sup>A. Makishima and T. Tani (unpublished).
- <sup>14</sup>T. Tani and A. Makishima (unpublished).
- <sup>15</sup>J. Friedrich, J. Swalen, and D. Haarer, J. Chem. Phys. 73, 705 (1980).
- <sup>16</sup>J. M. Hayes and G. J. Small, Chem. Phys. 27, 151 (1978), Chem. Phys. Lett. 54, 435 (1978).
- <sup>17</sup>S. Völker, R. M. MacFarlane, A. Z. Genack, H. P. Trommsdorff, and H. J. van der Waal, J. Chem. Phys. 67, 1759 (1977).
- <sup>18</sup>J. Friedrich, H. Wolfrum, and D. Haarer, J. Chem. Phys. 77, 2309 (1982).
- <sup>19</sup>T. Tani, H. Anzai, U. Itoh, and T. Moriya, Meeting of Phys. Soc. Jpn. (Nov. 1984) 5p-TC-2, Meeting of Mol. Struc. (Oct. 1984) 1C08, and also to be presented in XII International Conference of Photochemistry (Aug. 4-9, 1985, Tokyo).
- <sup>20</sup>M. Nogami and Y. Moriya, J. Non-Cryst. Solids 37, 191 (1980).
- <sup>21</sup>S. K. Lyo and R. Orbach, Phys. Rev. B 22, 4223 (1980).
- <sup>22</sup>O. L. Anderson and H. E. Bömmel, J. Am. Ceram. Soc. 38, 125 (1955).
- <sup>23</sup>S. Hunklinger and W. Arnold, in *Physical Acoustics*, Vol. 12, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1976).
- <sup>24</sup>W. A. Phillips (Ed.), *Amorphous Solids* (Springer, Berlin, 1981).
- <sup>25</sup>K. M. Sinnott, J. Polym. Sci. 35, 273 (1959).
- <sup>26</sup>K. M. Sinnott, J. Polym. Sci. 42, 3 (1960).
- <sup>27</sup>K. Shimizu, O. Yano, and Y. Wada, J. Polym. Sci. Polym. Phys. Ed. 2, 1641 (1973).
- <sup>28</sup>H. P. H. Thijssen, A. J. M. Dicker, and S. Völker, Chem. Phys. Lett. 92, 7 (1982).

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Plasma exposure to the solid sample of viologen was performed in a 25-mL Erlenmeyer flask. The sample was then mixed with degassed DMF and the spectra measured.

ESR spectra were measured on a quartz probe at room temperature using JES-FEIX spectrometer (Nippon Denshi Ltd.).

**Acknowledgment.** This research was supported in part by the Grant-in-Aid from the Ministry of Education, Science, and Culture, Japan, No. 455351 (1979). The authors are grateful to Professors Y. Kurimura (Tharaki University) and E. Tsuchida

(Waseda University) for useful discussions and to Drs. A. Yamada and M. Kaneko (The Institute of Physical and Chemical Research) for the measurement of the ESR spectra and encouragement. Thanks are due to Mr. M. Takase and K. Honda for their experimental help.

Registry No. BV<sup>†</sup>, 1102-19-8; BV-Br, 27768-49-6; MV, 1910-42-5; BuV-Br, 32449-18-6; PVX, 31586-11-0; 60-4; BG, 633-03-4; DPPH, 1898-66-4; 4,4'-bipyridine-1,4-dimethylbenzene copolymer, 31533-65-0.

## The Nature of the Silica Cage As Reflected by Spectral Changes and Enhanced Photostability of Trapped Rhodamine 6G

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Rhodamine 6G was embedded in a matrix of silica gel glass by the sol to gel technique. The special features of an inorganic oxide glass as a carrier of an organic dye are discussed in comparison with other solid environments, such as adsorption on powders and within porous glasses, thin films, and doping of plastic matrices. Among the advantages mentioned are photostability of the glass matrix, trapping of the dye molecule, and its total isolation from undesired interactions with its neighbors, dye molecules, impurities, and photodecomposition products; nonleachability of the dye; the ability to reach stable very high dye concentrations; reduction of translational, rotational, and vibrational degrees of freedom of the trapped dye; good transparency down to the UV. Embedding R6G in the silica glass enables one to reach high concentrations without undesirable dye aggregation. Stokes shift is larger in the glass than in water. Photostability of the dye is higher in the glass than in water. A remarkable front-face fluorescence stability is observed. These observations, and a critical review of the literature, are used to discuss the nature of the silica glass cage: it is suggested that it is a hydroxylc polar environment, though somewhat less polar than water. The rigidity of the cage is discussed in terms of required reorientation of the environment around an excited dye.

### Introduction

Organic laser dyes have found in the past two decades an increasing variety of applications in spectroscopy, in optics, and in lasers. Rhodamine 6G (R6G) has been one of the most frequently used probes in these studies, due to its high quantum yield of fluorescence, absorption and emission in the visible 500–600-nm range, and good laser properties.<sup>1</sup>

One of the key problems in the investigation and application of organic laser dyes is the matrix which hosts the dye. This is not surprising, since the nature of the matrix affects virtually all characteristics of the dye, e.g., it causes spectral shifts of both absorption and emission, it affects photostability, and it alters the distribution between processes the excited state may undergo, such as intersystem crossing, collisional energy loss, and consequently also fluorescence lifetime.<sup>1</sup>

Special attention has been given to solid matrices, including solid solutions, in contradistinction to fluid environments. The solid environments used to carry R6G as well as other fluorescent organic dyes may be grouped into four categories: (a) high surface area powdered materials in slurries or as colloids,<sup>2</sup> such as our recent study of R6G adsorbed on clays,<sup>3</sup> (b) high surface area porous glasses,<sup>4,5</sup> such as our study of fluorescent organometallic compounds adsorbed on Vycor porous glass and on disks of compressed fumed silica,<sup>6</sup> (c) polymeric blocks and thin films in which the dye is homogeneously distributed,<sup>7,8</sup> (d) monolayers and submonolayers of low surface area supports.<sup>9</sup> Here we wish to describe yet another solid matrix offering several unique features, namely, an *inorganic oxide glass* within which the dye is embedded. Recent developments in the low-temperature sol-gel process of oxide-glass preparations<sup>10,11</sup> opened the possibility to

use these superior materials instead of organic carriers. Specifically we report here some preliminary observations made on system R6G<sup>+</sup>Cl<sup>-</sup>/silica gel glass. Of special interest is the increase in fluorescence stability, the lack of aggregation at a concentration of 10<sup>-4</sup> M and higher, the increase in Stokes shift, and the UV transparency of the matrix. Unexpectedly, the rate of decrease in front-face fluorescence intensity of the doped glass was lower than the rate of absorption fading.

### Advantages of the New Solid Dye Carrier

We list now a number of advantages in using an inorganic glass as a carrier for organic dyes, in comparison to fluid media:

- (1) F. P. Schäfer, Ed., "Dye Lasers", 2nd ed, Springer, Berlin, 1981.
- (2) E.g., J. Wheeler and J. K. Thomas, *J. Phys. Chem.*, **86**, 4510 (1982); N. Furlong, *Aust. J. Chem.*, **35**, 911 (1982).
- (3) Z. Grauer, D. Avnir, and S. Yaniv, *Can. J. Chem.*, in press.
- (4) (a) S. Wi and H. D. Gafney, *Chem. Phys. Lett.*, **99**, 253 (1983); (b) Wolfgang and H. D. Gafney, *J. Phys. Chem.*, **87**, 5395 (1983).
- (5) (a) V. I. Zemskii, I. K. Meshkovskii, and A. V. Sechikarev, *Sov. Dokl.*, **27**, 1047 (1982); (b) G. B. Altshuler, E. G. Sulneva, L. K. Meleshko, and K. I. Kirillov, *Zh. Prikl. Spektrosk.*, **36**, 592 (1982); (c) G. B. Altshuler, V. Bakhanov, E. G. Dulneva, and J. K. Meshkovskii, *Opt. Spektrosk.*, **59**, 1029 (1983); (d) V. I. Zemskii and I. K. Meshkovskii, *Pisma Zh. Tekh. Kibernetiki*, **10**, 1029 (1983).
- (6) R. Reisfeld, N. Manor, and D. Avnir, *Solar Energy Materials*, **1**, 1 (1983).
- (7) N. S. Allen and J. F. McKellar, Ed.; "Photochemistry of Dye-Pigmented Polymers", Applied Science Publishers, London, 1980.
- (8) R. Reisfeld and C. K. Jorgensen, *Structure Bonding*, **49**, 1 (1983).
- (9) E.g., T. F. Heinz, C. K. Chen, D. Ricard, and Y. R. Shen, *Phys. Lett.*, **48**, 478 (1982); S. Garoff, R. B. Stephens, C. D. Hanson, and J. Sorensen, *J. Lumines.*, **24/25**, 773 (1981); S. Garoff, D. A. Weitz, and J. Alvarez, *Chem. Phys. Lett.*, **93**, 283 (1982); Y. Liang, A. M. P. Goncalves, and D. K. Negus, *J. Phys. Chem.*, **87**, 1 (1983).
- (10) H. Dialich, *J. Non-Cryst. Solids*, **57**, 371 (1983).
- (11) M. Yamane, S. Aso, and T. Sakano, *J. Mater. Sci.*, **13**, 865 (1983).

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### Silica Glass

Using the solid matrices described above, Rhodamine 6G molecules have no translational freedom for the dye. Intermolecular interactions which could lead to dimerization is thus avoided. Each molecule is trapped in a rigid cage.

Any residual impurities in the dye are isolated and do not interfere with the photoactive (photo) processes. Embedding the dye in the glass facilitates effective purification of the dye.

Similarly, photodecomposition products do not migrate and facilitate further photodecomposition.

Unlike permeable organic plastics, and unlike adsorbed dyes, the molecule of interest is totally isolated from surrounding gas, liquid, or polymeric environments.

A severe limitation of plastic carriers<sup>7</sup> and organic solvents<sup>12</sup> is their low photostability and low thermal stability. Silica glass is photochemically and can tolerate heat well above organic solution temperatures.

The doped glass is nonleachable (see below). Leachability is a problem in films or in porous supports which carry the dye at the surface.

The solid cage reduces internal rotational modes in the dye, probably to a greater extent than the relatively flexible organic polymer molecules. Rotational relaxation of the excited state of the dyes is one of the main modes of nonradiative energy loss.<sup>13</sup> The separation of the dye molecules from each other enables one to reduce the quenching of conventional high dye concentration, without changing the environment, from the points of view of chemical concentration and probability of deactivation processes (e.g., aggregation and translational collision). In other words, optical constants such as reabsorption processes, become isolated from high-concentration interferences.

Plastics absorb in the near-UV; the above-mentioned high scatter in this range. Our silica glass is devoid of these obstacles (Figure 1) well beyond the visible range. A result of this is the desired geometry is easily obtainable either at the synthesis stage or by manipulation on the final glass.

### Experimental Section

Monolithic silica gel glasses were prepared by basic hydrolysis of  $\text{Si}(\text{OMe})_4$ , followed by slow (1 week) condensation at room temperature following the procedure of Drexhage.<sup>11</sup> R6G<sup>-Cl</sup><sup>-</sup> was added prior to gelation. The monolithic glass in the form of a disk, 2 cm in diameter, 1 mm thick, was further dried for 24 h at 65 °C to remove water and methanol. Front-phase fluorescence ( $\lambda_{\text{ex}}$ ) was measured on an Aminco-SLM spectrofluorimeter. Emission spectra were recorded on a Cary-219 spectrometer. Photooxidation was carried out by placing the samples in a quartz cell (1 cm) of a 1.6-kW halogen-quartz lamp, with proper filtering of <300 nm. Radiation dosage as measured inorganic phosphate spectrophotometer was 65.2 mW/cm<sup>2</sup>.

### Results and Discussion

**Transparency due to the Small Size of the Cages.** The glass made by the sol-gel process is porous. However, the pore radii are smaller (1.5–10 nm)<sup>11</sup> than the near-UV or visible wavelength. The cages are probably even smaller than 1 nm (see section 3 below). Consequently, the glass is transparent (Figure 1). In comparison, the commonly used dye carrier, i.e., monomer (polymethylmethacrylate), filters light <330 nm.

**Leachability from the Cage.** It was important to establish whether the dye molecules are indeed incorporated within the bulk and not adsorbed at the exposed walls of the pores.

For comparison purposes, an undoped porous gel glass was prepared and R6G then adsorbed onto its surface, as previously reported.<sup>1</sup> A doped gel glass and an adsorbed glass were then leached in two leaching solvents: water and methanol.

Shen, Fletcher, Kippe, and Pitrak,<sup>14</sup> and Drexhage,<sup>15</sup> have shown the difference between adsorbed and solvated R6G was reached (faster with methanol, slower with water) in the case of the Weitz, and M. P. Goran,<sup>16</sup> and Weitz,<sup>17</sup> respectively.

A. N. Fletcher, R. H. Kippe, and M. E. Pitrak, *Appl. Phys. B*, **27**,

**13, 865 (1977);** A. N. Fletcher and R. H. Drexhage, *Laser Focus*, **35**, (March 1973).

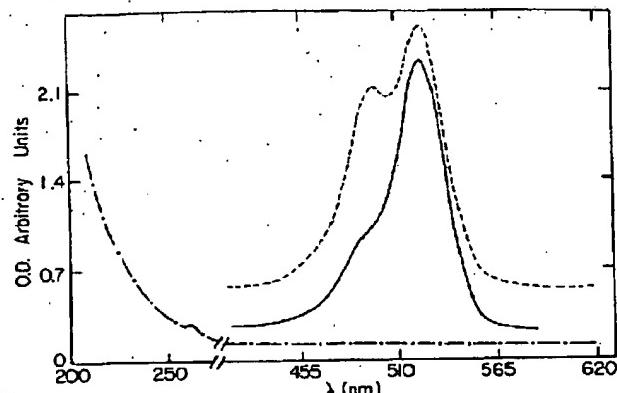


Figure 1. Absorption spectra of rhodamine 6G: (---)  $1.4 \times 10^{-4}$  M in water. The dimer is clearly visible at 496 nm. (—)  $1.6 \times 10^{-4}$  M in gel glass; (- -) undoped glass.

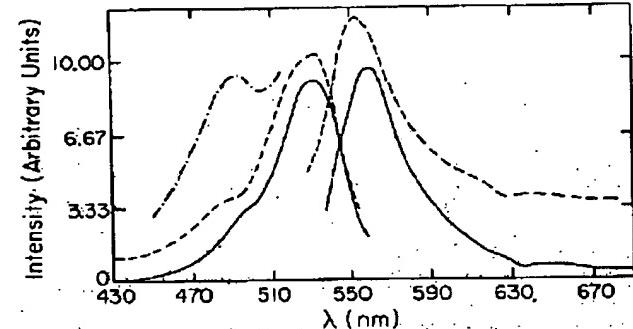


Figure 2. Emission and excitation ( $\lambda_{\text{ex}} = 523$  nm) spectra of rhodamine 6G (---) in solution ( $1.4 \times 10^{-4}$  M) and (—) in gel glass ( $1.6 \times 10^{-4}$  M). The dimer (—) is reproduced from Figure 1 for comparison purpose.

adsorbed glass, and the solvents were strongly colored. No detectable (by eye or by instrument) leakage of R6G was observed from the doped glass. It is thus established that R6G is either completely trapped in a surrounding rigid cage or that R6G molecules are trapped in bottleneck pores,<sup>14</sup> with rigid pore entrances of diameter smaller than the effective diameters of methanol or water ( $\sim 4$  Å).<sup>15</sup>

**3. Lack of Dimerization as Reflecting Some Properties of the Cage.** The dimerizations and aggregations of laser dyes have gained an intensive and on-going study because of the strong effects of these processes on spectral and lasing properties. At  $10^{-4}$  M, in water, R6G is not lasing due to dimerization.<sup>16</sup> Much controversy exists on the question of whether R6G dimers fluoresce<sup>17–19</sup> or not.<sup>16,20</sup> It seems to us that the bulk of evidence agrees with Levshin's old conclusion (1927<sup>21</sup>) that dye aggregation is the basic cause for concentration quenching of dye luminescence. Drexhage pointed out<sup>16</sup> that not only do these aggregates not fluoresce but they also reabsorb fluorescence from the monomer. Chibisov and Slarnova have shown<sup>18</sup> that fluorescence quenching in R6G aggregates is mainly due to efficient intersystem crossing.

In view of all this, we found it of advantage that, when embedded in our glasses, R6G does not aggregate much beyond the limit of  $10^{-4}$  M (moles of dye per liter glass) (e.g., Figure 1). A

(14) K. Unger, "Porous Silica", Elsevier, Amsterdam, 1979.

(15) A. L. McClellan and H. F. Harmberger, *J. Colloid Interface Sci.*, **57**, (1976).

(16) K. H. Drexhage, Chapter 4 in ref 1.

(17) J. E. Selwin and J. I. Steinfield, *J. Phys. Chem.*, **76**, 762 (1972).

(18) A. K. Chibisov and T. D. Slarnova, *J. Photochem.*, **8**, 285 (1978).

(19) S. L. Chin, N. Leclerc, and G. Bedard, *Opt. Commun.*, **6**, 264 (1972).

(20) V. L. Levshin and L. V. Krotova, *Opt. Spectrosc.*, **11**, 457 (1962);

E. G. Baranova and V. L. Levshin, *Opt. Spectrosc.*, **10**, 182 (1961), and references cited therein.

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similar deaggregation effect was observed when R6G was adsorbed on the surface of the porous glass, at least up to  $10^{-3}$  M (or when adsorbed on smectite clays<sup>21</sup>). Lack of aggregation is also evident from the excitation spectrum of the doped glass (Figure 2). In solution, deaggregation of R6G may be achieved by using organic solvents,<sup>20,22</sup> mixtures of water and organic solvents,<sup>20</sup> and various water-soluble organic additives.<sup>16</sup> However, unlike silica glass, all these organic media are photolabile and actively participate in photodegradation processes.<sup>12</sup>

The fact that in the glass R6G does not aggregate may shed some light on the nature of the local environment of the dye, although, as was the case with the question of aggregate fluorescence, controversy still exists on the role of water in causing aggregation.<sup>16</sup> Special attention was given to solvent dielectric constants as a stabilizing force, reducing Coulombic repulsion.<sup>23</sup> However, as pointed out correctly by Rohatgi and Singhal,<sup>24</sup> the (unknown) microscopic dielectric constant around the dye and not the bulk constant should be of interest. Arvan and Zaitseva<sup>25</sup> clearly demonstrated this point. Following Drexhage and Reynold's argumentation,<sup>26</sup> it seems to us that much of the published experimental data points to a picture in which the higher the hydrophobicity of the dye, the greater its tendency to form aggregates. Consequently, a polycationic organic species, such as the R6G dimer cation, is more easily watersoluble than a monocationic organic species.

Two types of silicon groups probably form the walls of the silica glass cage: silanols ( $\text{Si}-\text{OH}$ ) and siloxanes ( $\text{Si}-\text{O}-\text{Si}$ ).<sup>14</sup> Both groups are indeed of lower polarity and higher hydrophobicity than water. Leermakers has measured<sup>27</sup> the Kossoower Z value<sup>18</sup> of silica gel and found  $Z = 88$ , which is in between the values for methanol and water. The hydrophobicity of siloxane surfaces is well established.<sup>28</sup> For R6G attached to siloxane planes in clays we found an effective polarity resembling the lower-chain alkanols as reflected in absorption maxima red shifts.<sup>3</sup> The silica cage is, however, probably rich in silanols (and perhaps few residual physisorbed water molecules) as judged from the fact that no such red shift in  $\lambda_{\text{max}}$  compared to water (525 nm) is observed. Taking into account Leermaker's measurement<sup>27</sup> and Chou et al.<sup>22</sup> measurements in which water and methanol gave the same  $\lambda_{\text{max}}$ , we feel that, if a comparison to solvents is desired, the cage may be regarded as a hydroxylc, relatively polar environment, less polar than water.

The fact that no dimers are observed may serve as an indication to the size of the cage: roughly that of a single molecule, i.e., 10 Å; otherwise, sufficient water would be trapped (a) to form dimers at the high dye concentration employed and (b) to remove the dye from the cage wall as indicated by the experiment of leaching the adsorbed dye, so that the fluorescence would not have been red-shifted compared to water (next section).

**4. Cage Rigidity and Fluorescence Red Shift.** Red shifts (5–10 nm) have been observed for the emission maximum (Figure 2). This desirable increase in Stokes shift (from 30 to 40 nm) may shed more light on the nature of the silica cage. In most cases spectral shifts in fluorescence maxima are associated with the effects of solvent molecules having sufficient time to reorient themselves around an equilibrium excited state. This new orientation is different from the solvent cage of the ground state and the corresponding Franck-Condon excited state.<sup>30</sup> A silica glass cage is unique in that the only possible reorientation of the cage walls are rotations around the  $\text{Si}-\text{O}-\text{H}$  bonds, i.e., relocation of

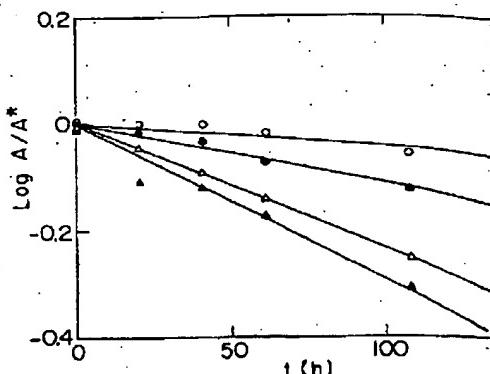


Figure 3. Photodecomposition of rhodamine 6G.  $A/A^*$  is the relative decrease in intensity of either absorption ( $\Delta$  in water,  $\bullet$  in glass) or emission ( $\triangle$  in water,  $\circ$  in glass). Concentration in water:  $10^{-3}$  M; in glass:  $1.5 \times 10^{-4}$  M. All fluorescence measurements, including water, were by front-face geometry, and comparison to  $t = 0$  ( $A^*$ ) carried out repeatedly for each point. See also Table I.

TABLE I: Rhodamine 6G Absorption and Fluorescence Parameters

	$t_{1/2}, \text{ h}$	$k, 10^{-3} \text{ h}^{-1}$
fluorescence in water	86	$8.11 \pm 0.10$
absorption in water	111	$6.25 \pm 0.10$
fluorescence in glass	622	$0.11 \pm 0.01$
absorption in glass	235	$2.95 \pm 0.05$

hydrogen bonding to the dye. Under this restricted cage, the rotational movements of the molecule, rather than the surroundings, become important in excited-state stabilization and interactions with the cage. As discussed above, the cage walls are less polar than water; this was further corroborated by a fluorescence red shift, such as observed also in nonpolar solvents.<sup>1</sup> These red shifts may be interpreted as reflecting changes in the dipole moment of the excited molecule.<sup>30</sup> Apparently, the restricted motions of the silica walls and of the dye are responsible for the desired stabilizing mutual reorientation.

**5. Absorption and Fluorescence Photostability.** It is to be expected, in view of the material presented so far, that there is an increase in photostability: trapping of the dye molecule in the cage, photodecomposition products, and other impurities; desorption, and reduction of both vibrational and rotational modes; and energy dissipation all contribute to the enhanced stability. Comparing the first-order decomposition<sup>3,31</sup> analysis, under the conditions described in the Experimental Section, revealed the data shown in Table I and in Figure 3. In water, the fluorescence intensity decreases faster than absorption intensity. This is due to the sensitivity of fluorescence to a steady increase of photodecomposition products. In glass, however, this order is reversed: the fluorescence intensity decrease is much slower than the absorption intensity decrease. This interesting phenomenon may be understood by noticing that, in the bleaching process, the dye is transformed into colorless products.<sup>31</sup> Therefore, in glass, the glass fluorescence by a front-face geometry, new dye molecules, of undestroyed R6G molecules are constantly exposed, and the emission is not blocked by the transparent photodecomposition products which are trapped in the upper layers. The apparent renewability of doped glass layers, which amounts to an increase in the apparent fluorescence stability, seems to us to have important practical consequences such as for dye blocks for optical recording. Absorption spectroscopy, on the other hand, reveals an increase in the decrease in number of dye molecules along the measurement wavelength and hence the difference in apparent decrease in absorption photostability, compared to fluorescent measurements.

Comparative measurements by transmission fluorescence, at  $180^\circ$  or at  $90^\circ$ , are impossible at this preliminary stage.

(31) I. P. Kaminov, L. W. Stutz, E. A. Chandross, and C. A. Miller, *J. Opt. Soc.*, **7**, 1563 (1972).

- (21) V. L. Levshin, *Z. Phys.*, **43**, 230 (1927).  
 (22) G. Chou and Z. Xingkang, *Acta Opt. Sin.*, **3**, 64 (1983).  
 (23) E.g., T. H. Förster and E. Konig, *Z. Electrochem.*, **61**, 344 (1957).  
 (24) K. K. Rohatgi and G. S. Singhal, *J. Phys. Chem.*, **70**, 1695 (1966).  
 (25) K. L. Arvan and N. B. Zaitseva, *Opt. Spectrosc.*, **10**, 137 (1961).  
 (26) Reference 1, p 159.  
 (27) P. A. Leermakers, H. T. Thomas, L. D. Weis, and F. C. James, *J. Am. Chem. Soc.*, **88**, 5075 (1966).  
 (28) E. M. Kossoower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).  
 (29) S. Yariv and H. Cross, "Geochemistry of Colloid Systems", Springer, Berlin, 1979.  
 (30) J. E. Bell in "Spectroscopy in Biochemistry", J. E. Bell, Ed., CRC Press, Florida, 1981, chapter 4.

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the high dye concentrations employed and due to scattering at the edges. Optical improvements are in progress.

The potential uses of fluorescent gel glasses in photoprocesses and other applications are numerous. Examples are light guides for lasers and optical fibers, luminescent solar concentrators and filters for linear and non-linear optics. These and other uses as well as the material discussed in this paper are patent pending.

**Acknowledgment.** We thank Zvi Grauer, N. Manor and H. Tzeboval for helpful discussions and technical assistance. This work was sponsored by the West-German Ministry of Science and Technology and assisted in part by the F. Haber Research Center for Molecular Dynamics, Jerusalem.

Registry No. Rhodamine 6G, 989-38-8; silica, 7631-86-9.

## Vibrational Spectroscopic Study of the Interlamellar Kaolinite-Dimethyl Sulfoxide Complex

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The intercalation complex involving the layer silicate kaolinite and dimethyl sulfoxide ( $\text{Me}_2\text{SO}$ ) is studied through the combined application of Raman and infrared absorption spectroscopy. The spectral data indicated that the  $\text{Me}_2\text{SO}$  molecules were in a restricted, highly ordered interlamellar conformation, with the oxygen of the sulfonyl group hydrogen bonded to OH groups in the gibbsite-sheet surface of kaolinite and the sulfur atom of the group keyed into the ditrigonal cavity on the opposing silicate surface of the mineral. The methyl group in the intercalated molecule appeared to be influenced by both of the opposing mineral surfaces to the extent that vibrational degeneracy in the CH stretching modes was lifted.

example for a comparative Raman-IR study because of the high stability of the complex relative to other kaolinite intercalation complexes,<sup>13</sup> the appearance of well-defined, discrete bands in the hydroxyl stretching region of the IR spectrum of the complex,<sup>14</sup> and the high Raman activity of many of the vibrational modes of  $\text{Me}_2\text{SO}^{21}$ .

True intercalation of  $\text{Me}_2\text{SO}$  into kaolinite, as opposed to multilayer adsorption on external surfaces, has been confirmed

- (1) T. J. Pinnavaia, *Science*, **220**, 365 (1983).
- (2) M. J. Tricker, D. T. B., Temmakiin, J. M. Thomas, and S. H. Graham, *Nature (London)*, **253**, 110 (1975).
- (3) J. M. Thomas in "Intercalation Chemistry", M. S. Whittingham and A. J. Jacobson, Eds., Academic Press, New York, 1982, Chapter 3.
- (4) M. B. McBride, *Clays Clay Miner.*, **25**, 6 (1976).
- (5) T. J. Pinnavaia in "Advanced Chemical Methods for Soil and Clay Minerals Research", J. W. Stucki and W. L. Banwart, Eds., D. Reidel, Dordrecht, 1980, p 391.
- (6) A. V. Kiselev and V. I. Lygin, "Infrared Spectra of Surface Compounds", Halsted Press, New York, 1975.
- (7) T. A. Egerton, A. H. Hardin, Y. Kozirovski, and N. Sheppard, *J. Catal.*, **32**, 343 (1974).
- (8) B. A. Morrow and A. H. Hardin, *J. Phys. Chem.*, **83**, 3135 (1979).
- (9) B. A. Morrow, *J. Phys. Chem.*, **81**, 2663 (1977).
- (10) H. Jeziorski and H. Knozinger, *J. Phys. Chem.*, **83**, 1166 (1979).
- (11) C. T. Johnston, Ph.D. dissertation, University of California, Riverside, CA, 1983.
- (12) G. S. Garcia and M. S. Camazano, *An. Edafol. Agrobiol.*, **24**, 495 (1965).
- (13) S. Olejnik, L. A. G. Aylmore, A. M. Posner, and J. P. Quirk, *J. Phys. Chem.*, **72**, 241 (1968).
- (14) O. Anton and P. G. Rouxhet, *Clays Clay Miner.*, **25**, 259 (1977).
- (15) J. M. Adams and S. Walli, *Clays Clay Miner.*, **28**, 130 (1980).
- (16) M. I. Cruz, A. Laycock, and J. L. White, *Proc. Int. Clay Conf.*, **1**, 775 (1969).
- (17) S. Olejnik, A. M. Posner, and J. P. Quirk, *Clays Clay Miner.*, **19**, 83 (1971).
- (18) S. Olejnik, A. M. Posner, and J. P. Quirk, *J. Colloid Interface Sci.*, **37**, 536 (1971).
- (19) R. L. Ledoux and J. L. White, *J. Colloid Interface Sci.*, **21**, 127 (1966).
- (20) S. Olejnik, A. M. Posner, and J. P. Quirk, *Spectrochim. Acta, Part A*, **27**, 2005 (1971).
- (21) M. T. Forel and F. Tranquille, *Spectrochim. Acta, Part A*, **26**, 1023 (1970).

<sup>1</sup> is the ratio of the intensity of the peak at  $1030 \text{ cm}^{-1}$  to that at  $1040 \text{ cm}^{-1}$ . <sup>2</sup> in glass. <sup>3</sup> in water:  $10^{-4} \text{ M}$ ; including water ( $4\%$ ) carried out.

<sup>4</sup> Photostability:  $10^{-3} \text{ h}^{-1}$ . <sup>5</sup>  $1 \pm 0.16$ . <sup>6</sup>  $5 \pm 0.02$ . <sup>7</sup>  $1 \pm 0.04$ . <sup>8</sup>  $5 \pm 0.07$ .

<sup>9</sup> cage (intercalant) <sup>10</sup> larger than  $10 \text{ Å}$  <sup>11</sup> stabilize <sup>12</sup> <sup>13</sup> <sup>14</sup> <sup>15</sup> <sup>16</sup> <sup>17</sup> <sup>18</sup> <sup>19</sup> <sup>20</sup> <sup>21</sup> <sup>22</sup> <sup>23</sup> <sup>24</sup> <sup>25</sup> <sup>26</sup> <sup>27</sup> <sup>28</sup> <sup>29</sup> <sup>30</sup> <sup>31</sup> <sup>32</sup> <sup>33</sup> <sup>34</sup> <sup>35</sup> <sup>36</sup> <sup>37</sup> <sup>38</sup> <sup>39</sup> <sup>40</sup> <sup>41</sup> <sup>42</sup> <sup>43</sup> <sup>44</sup> <sup>45</sup> <sup>46</sup> <sup>47</sup> <sup>48</sup> <sup>49</sup> <sup>50</sup> <sup>51</sup> <sup>52</sup> <sup>53</sup> <sup>54</sup> <sup>55</sup> <sup>56</sup> <sup>57</sup> <sup>58</sup> <sup>59</sup> <sup>60</sup> <sup>61</sup> <sup>62</sup> <sup>63</sup> <sup>64</sup> <sup>65</sup> <sup>66</sup> <sup>67</sup> <sup>68</sup> <sup>69</sup> <sup>70</sup> <sup>71</sup> <sup>72</sup> <sup>73</sup> <sup>74</sup> <sup>75</sup> 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<sup>606</sup> <sup>607</sup> <sup>608</sup> <sup>609</sup> <sup>610</sup> <sup>611</sup> <sup>612</sup> <sup>613</sup> <sup>614</sup> <sup>615</sup> <sup>616</sup> <sup>617</sup> <sup>618</sup> <sup>619</sup> <sup>620</sup> <sup>621</sup> <sup>622</sup> <sup>623</sup> <sup>624</sup> <sup>625</sup> <sup>626</sup> <sup>627</sup> <sup>628</sup> <sup>629</sup> <sup>630</sup> <sup>631</sup> <sup>632</sup> <sup>633</sup> <sup>634</sup> <sup>635</sup> <sup>636</sup> <sup>637</sup> <sup>638</sup> <sup>639</sup> <sup>640</sup> <sup>641</sup> <sup>642</sup> <sup>643</sup> <sup>644</sup> <sup>645</sup> <sup>646</sup> <sup>647</sup> <sup>648</sup> <sup>649</sup> <sup>650</sup> <sup>651</sup> <sup>652</sup> <sup>653</sup> <sup>654</sup> <sup>655</sup> <sup>656</sup> <sup>657</sup> <sup>658</sup> <sup>659</sup> <sup>660</sup> <sup>661</sup> <sup>662</sup> <sup>663</sup> <sup>664</sup> <sup>665</sup> <sup>666</sup> <sup>667</sup> <sup>668</sup> <sup>669</sup> <sup>670</sup> <sup>671</sup> 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